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Excitation energy dependent Raman spectrum of MoSe₂

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Raman investigation of MoSe₂ was carried out with eight different excitation energies. Seven peaks, including E_{1g} , A_{1g} , E_{2g}^1 , and A_{2u}^2 peaks are observed in the range of 100–400 cm⁻¹. The phonon modes are assigned by comparing the peak positions with theoretical calculations. The intensities of the peaks are enhanced at different excitation energies through resonance with different optical transitions. The A_{1g} mode is enhanced at 1.58 and 3.82 eV, which are near the A exciton energy and the band-to-band transition between higher energy bands, respectively. The E_{2g}^1 mode is strongly enhanced with respect to the A_{1g} mode for the 2.71- and 2.81-eV excitations, which are close to the C exciton energy. The different enhancements of the A_{1g} and E_{2g}^1 modes are explained in terms of the symmetries of the exciton states and the exciton-phonon coupling. Other smaller peaks including E_{1g} and A_{2u}^2 are forbidden but appear due to the resonance effect near optical transition energies.

Transition metal dichalcogenides (TMDCs) such as MoS₂ and MoSe₂ have been investigated for decades because of their layered 2-dimensional nature¹. Recently, few-layer TMDCs are attracting much interest as new 2-dimensional materials complementing graphene^{2,3}. Because most TMDCs are semiconductors with finite band gaps, they are expected to overcome the limitations of graphene stemming from the lack of a band gap while preserving the advantages of 2-dimensional materials. For example, a large on-off ratio exceeding 10⁶ and a high mobility have been achieved in MoS₂ and MoSe₂ field effect transistors^{2,4,5}. On the other hand, MoS₂ and MoSe₂ are important constituents in polycrystalline thin-film solar cells such as Cu(In,Ga)(S,Se)₂ and Cu₂ZnSn(S,Se)₄, which have Mo as the back contact layer. During the thin film deposition process, formation of a MoS₂ or MoSe₂ layer on top of the Mo back contact layer is inevitable. The thickness and fine structure of such a layer affect the performance of the solar cell significantly^{6–8}. Both MoS₂ and MoSe₂ have indirect band gaps for the bulk materials and become direct for monolayer. It should be noted, however, that the relative movements of the conduction and valence bands are reported to be different for different TMDC material^{9–13}.

Raman spectroscopy is a powerful tool to study the structural properties of graphene and 2-dimensional materials and is commonly used to determine the number of layers^{14–16}. For this purpose, it is important to understand the Raman spectra of bulk materials first, in order to make correct interpretations. In addition, resonance effects can be used to shed light on the electronic structure. For example, the Raman spectrum of MoS₂ shows a strong resonance effect and varies significantly with the excitation energy^{17,18}. Such effects have been interpreted in terms of resonances with exciton or exciton-polaritons in MoS₂. For MoSe₂, the resonance profiles of the main Raman modes of bulk MoSe₂ were carried out at liquid helium temperature in the range of 2.41–2.71 eV in order to obtain the resonance profile with a high resolution^{19,20}. It was found that the Raman intensities of both A_{1g} and E_{2g}^1 phonons are enhanced at A, B, A', and B' exciton levels. It was also found that near the band-to-band transition at ~2.5 eV, the Raman intensity of the A_{1g} phonon is enhanced, whereas that of the E_{2g}^1 phonon is not^{19,20}. However, the variation of the spectrum as a function of the excitation energy was not presented. More recently, the thickness dependence of the main modes in few-layer MoSe₂ in the range of 230–360 cm⁻¹ was studied for 1 to 5 layers and bulk with the excitation energy of 2.41 eV²¹. However, unlike the case of MoS₂, a comprehensive Raman study on MoSe₂ has been lacking. For thin-film solar cells, Raman is used to study the formation and structures of secondary phases such as MoS₂ or MoSe₂. In the Raman spectrum of thin-film Cu₂ZnSn(S,Se)₄, for example, the

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Figure 1. (a) Top view and (b) side view of 2H-MoSe₂.

A_{1g} and the A_{2u}^2 peaks of MoSe₂ overlaps those due to ZnSe and ZnS secondary phases^{22,23}, respectively, making it difficult to identify the secondary phases in the film. By choosing an appropriate excitation energy matching resonance conditions, one can selectively enhance the signal from MoSe₂ and unambiguously identify the existence of MoSe₂ in Cu₂ZnSn(S,Se)₄.

Here we present Raman studies on bulk MoSe₂ using eight different excitation energies in the range of 1.6–3.8 eV. We found that the Raman spectrum changes dramatically at excitation energies near resonance with exciton states²⁴ because different modes are enhanced at different resonances. The results would provide a foundation on Raman studies of few-layer MoSe₂.

Results and Discussion

The crystal structure of 2H-MoSe₂ is shown in Fig. 1. Consecutive layers are stacked such that the Mo and Se atoms form a hexagonal arrangement in the top view as in Fig. 1(a). The point group of bulk 2H-MoSe₂ is D_{6h}^4 , and there are 12 vibration modes at the center of the Brillouin zone, expressed as^{19,25}

$$\Gamma = A_{1g} + 2A_{2u} + B_{1u} + 2B_{2g} + E_{1g} + 2E_{1u} + 2E_{2g} + E_{2u}. \quad (1)$$

A_{2u}^1 and E_{1u}^1 are acoustic modes, A_{2u}^2 and E_{1u}^2 are infrared active modes, A_{1g} , E_{1g} , E_{2g}^1 , and E_{2g}^2 are Raman active modes, and the rest are inactive¹. The Raman tensors¹⁹ are expressed with respect to $X = [100]$, $Y = [010]$, and $Z = [001]$ as

$$A_{1g} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}, \quad E_{1g} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & c \\ 0 & c & 0 \end{pmatrix}, \quad \begin{pmatrix} 0 & 0 & -c \\ 0 & 0 & 0 \\ -c & 0 & 0 \end{pmatrix}, \quad (2)$$

and

$$E_{2g} = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (3)$$

In the backscattering geometry, E_{1g} modes are forbidden.

Figure 2 shows the Raman spectra for different excitation energies, normalize to the intensity of the peak at 242 cm⁻¹, which is present in all the spectra. The most prominent peaks are the Raman active A_{1g} and E_{2g}^1 modes¹⁹ at 242 and 285 cm⁻¹, respectively. It is evident that these two modes have different excitation energy dependences as seen in Fig. 3(a). In order to further compare the excitation dependences of these two peaks, the intensities of the two peaks as well as their ratio are plotted as functions of the excitation energy in Fig. 3(b). In order to correct for the throughput of the measurement system, the intensities for different excitation energies were calibrated with the 520 cm⁻¹ signal from the Si substrate accounting for the resonance Raman curve of Si²⁶.

The A_{1g} peak is strong at the lowest and the highest excitation energies of 1.58 and 3.82 eV, respectively, with the minimum at 2.71 eV. On the other hand, the E_{2g}^1 peak is almost invisible at low excitation energies and increases monotonically at excitation energies above 2.54 eV. The excitation energy dependence of the Raman peak intensity is analyzed in terms of the resonance Raman effect. For bulk MoSe₂, the indirect gap is located close to 1.1 eV whereas the lowest direct transition is around 1.5 eV. For optical processes, however, since the excitonic effect significantly modifies the optical spectrum, the exciton states should be considered²⁷. Optical transmission measurements estimated the energies of the A, B, and C exciton states of bulk MoSe₂ at 1.6, 1.8, and 2.8 eV, respectively^{24,28}. Therefore,

Figure 2. Raman spectra of a bulk MoSe₂ with different excitation energies. The intensity was normalized by the intensity of A_{1g} mode of each spectrum. The sharp peaks below 150 cm⁻¹ for the 2.71-eV excitation are due to molecular vibration modes of air.

Figure 3. (a) Raman spectra of bulk MoSe₂ taken with the excitation energies indicated. (b) Intensities of A_{1g} and E_{2g}¹ modes and E_{2g}¹/A_{1g} ratio as functions of the excitation energy. Some major optical transition energies²⁴ are indicated by capital letters.

the excitation energy dependence of the A_{1g} peak can be understood in terms of the ordinary resonance effect. The relative enhancement of the E_{2g}¹ peak for the excitation energies of 2.71 and 2.81 eV, however, calls for a special attention. Recently, Carvalho *et al.*¹⁸ reported a similar effect in resonance Raman studies of MoS₂. They observed that unlike the A_{1g} peak, the E_{2g}¹ peak exhibits a strong enhancement at the energy of the C exciton, which is associated with the transition between the top of the valence band and the first three lowest conduction bands near the Γ point. This peculiar difference between A_{1g} and E_{2g}¹ modes was interpreted in terms of the symmetry of the atomic orbitals contributing to the exciton states and symmetry-sensitive exciton-phonon coupling. In MoSe₂, on the other hand, Beal *et al.*²⁴ interpreted a sharp feature at ~2.84 eV in the optical transmission spectrum as a band-to-band transition between higher energy bands. However, it is more reasonable to interpret this transition at ~2.84 eV as being due to the C exciton in MoSe₂ because the peculiar resonance behavior of the E_{2g}¹ mode and the lack thereof for the A_{1g} mode are very similar to what was observed in MoS₂. Although there are differences in the band structures of MoS₂ and MoSe₂, the general features of the C exciton should be fairly similar and so the observed peculiar resonance of the E_{2g}¹ mode can be interpreted similarly.

E_{exc} (eV)	a	E_{1g}	b	A_{1g}	c	E_{2g}^1	d	A_{2u}^2
	E_{2g}^1 –LA at M		B_{1u}		$2E_{2g}^2$ at M			
cal ²⁹	281–136 = 145	170	240	242	$2 \times 124 = 248$	284.5	$181 + 136 = 317^a$ $2 \times 157 = 314^b$	344
1.58	139.9	167.6	—	242.0	249.3	285.0	313.8	—
1.96	139.5	167.3	—	242.0	249.3	285.4	315.0	—
2.33	—	168.0	—	242.0	249.2	284.8	317.1	—
2.41	—	168.8	—	242.0	249.4	284.4	—	352.8
2.54	—	168.8	—	242.0	249.4	284.4	—	352.2
2.71	146.5	168.9	238.6	242.0	249.4	284.2	—	352.7
2.81	144.3	168.2	—	241.9	249.3	285.5	—	352.9
3.82	—	—	—	241.7	not resolved	284.7	—	351.9

Table 1. Comparison of calculated vibrational modes with Raman peak positions in cm^{-1} for different excitation energies. ^aSum of E_{1g} and LA branches at the M point. ^b2-phonon frequency of the B_{2g} branch at the M point.

In addition to the main peaks, several fine features are clearly resolved in the frequency range from 100 to 650 cm^{-1} . The measured peak positions are compared with theoretical calculations by Ding and Xiao²⁹ to assign the phonon modes. The assignments are summarized in Table 1.

The peaks at 169 cm^{-1} is assigned to the E_{1g} mode. This mode is forbidden in backscattering but appears due to the resonance effect. Since the E_{1g} mode is an in-plane vibration mode similar to the E_{2g}^1 mode, its coupling with the C exciton state would be strongly enhanced, leading to the selection rule breaking near the resonance with the C exciton state. The selective enhancement of the infrared active and Raman forbidden A_{2u}^2 peak at 353 cm^{-1} cannot be explained in the same manner. This peak was measured in infrared measurements¹⁹ as well as in a recent Raman measurement with the 442-nm excitation⁵. When the excitation energy is close to the exciton energy, strongly localized exciton wavefunction effectively breaks the symmetry of the system, which in turn activates the modes that are normally Raman inactive. Similar symmetry breaking due to resonance with a strongly localized state was observed in nitrogen doped GaAs³⁰. Therefore, we interpret it's the enhancement of this peak as being due to the resonance-induced symmetry breaking.

We also attempt to analyze weaker features, labelled a , b , c , and d . Because the peak positions do not match any possible first order Raman processes, these features are interpreted as being due to second order Raman processes. Its appearance correlates with that of the multiple phonon peaks d and similar peaks at higher energies discussed below. Its frequency is close to that of Stokes-anti-Stokes pair of E_{2g}^1 –LA at the M point. Similar features were observed in Raman scattering of MoS_2 as well¹⁷. The peak b at 238 cm^{-1} appears as a shoulder for the 2.54 and 2.81 eV excitations and is well resolved for the 2.71 eV excitation. For all the other excitation energies, it is not resolved. The frequency difference between this peak and the A_{1g} mode is 3 cm^{-1} . Sekine *et al.*¹⁹ calculated the Davydov splitting of MoSe_2 using a simple spring model with two layers per unit cell and found its value to be $\sim 2 \text{ cm}^{-1}$, which is in line with more recent calculations²⁹. Therefore, we interpret this peak as the B_{1u} mode. Tonndorf *et al.*²¹ observed similar splitting in Raman spectra of 3–5 layer MoSe_2 , measured with the 2.41-eV excitation. In addition to the A_{1g} mode, the peak c at 248 cm^{-1} is observed for all excitation energies. This peak has not been analyzed in previous studies. The position of this peak is close to the calculated two-phonon energy of the E_{2g}^2 shear mode at the M point (248 cm^{-1}). For the 1.58-eV excitation, a broad peak labelled d and similar peaks at higher frequencies are observed. These peaks are multiple-phonon scattering peaks involving zone boundary phonons. For example, the frequency of the peak d , 315.3 cm^{-1} , is close to the sum of the E_{1g} (181 cm^{-1}) branch and the LA (136 cm^{-1}) branch or the 2-phonon frequency of the B_{2g} (314 cm^{-1}) branch at the M point. Similar multiple phonon peaks appear for the 2.71 and 2.81 eV excitations. In MoS_2 , similar peaks due to 2-phonon scattering appear near resonances¹⁷, and we interpret these peaks also as being due to 2-phonon scattering activated by the resonance effect.

In summary, we have shown that the Raman spectrum of MoSe_2 varies greatly with the excitation energy. The enhancements of the Raman peaks are explained in terms of the resonance with various optical transitions including different types of exciton states. Different symmetries of the exciton states and the exciton-phonon coupling can explain selective enhancement of particular phonon modes for some excitation energies. Moreover, based on our results, we propose to use excitation energies in the range of 2.54–2.81 eV to take advantage of the resonant enhancement of the E_{1g} or E_{2g}^1 peaks for detection of MoSe_2 secondary phases in thin film solar cell materials.

Methods

A single-crystal 2H-type bulk MoSe₂ flake bought from HQ Graphene was measured by micro-Raman spectroscopy. For the Raman measurement, we used 8 different excitation sources: the 325- and 441.6-nm (3.82 and 2.81 eV) lines of a He-Cd laser; the 457.9-, 488-, and 514.5-nm (2.71, 2.54, and 2.41 eV) lines of an Ar⁺ laser; the 532-nm (2.33 eV) line of a diode-pumped-solid-state laser; the 632.8-nm (1.96 eV) line of a He-Ne laser; and the 784.8-nm (1.58 eV) line of a diode laser. The laser beam was focused onto the flake by using a 50× objective lens (0.8 N.A.) for all excitation wavelengths except for the 325-nm excitation for which a 40× objective lens (0.5 N.A.) was used. The scattered signal was collected by the same objective lens (backscattering geometry) and was dispersed with a Jobin-Yvon Horiba iHR550 spectrometer. Either a 1200-grooves/mm (630-nm blaze) or a 2400-grooves/mm (400-nm blaze) grating was chosen to acquire the best signal to noise ratio. A liquid-nitrogen-cooled back-illuminated charge-coupled-device detector was used, and thin-film interference filters (RazorEdge Filters) from Semrock were used to reject the Rayleigh-scattered light. The laser power was kept at 100 μW for all the measurement to avoid local heating of the sample. The spectral resolution was below 1 cm⁻¹.

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Author Contributions

D.N. and J.-U.L. conducted the measurements. D.N., J.-U.L. and H.C. analyzed the data and discussed the results. All authors wrote the manuscript together.

Additional Information

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